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A RESONANCE RAMAN SCATTERING STUDY OF VIBRATIONAL DEPHASING IN THE MIXED CRYSTAL OF PENTACENE IN NAPHTHALENE

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Resonance Raman scattering is used to investigate vibrational dephasing in the mixed crystal of pentacene in naphthalene. It is shown that, as for the pure electronic transition, uncorrelated resonant phonon scattering processes in the ground and vibrationally excited state induce vibrational dephasing in this system.

1. Introduction

In recent years much work has been done aimed at a better understanding of vibrational dephasing in liquids [1] and pure molecular solids [2]. We mention here, for this presentation in particular, the spontaneous Raman scattering study by Harris and co-workers [2], of the line shape of the C–H(D) stretch vibration in durene (d_{14}). The observed exponential activation of both the Raman line width and frequency were interpreted by Harris et al. using exchange theory [2,3]. An unsolved problem with this interpretation is that the lifetime (τ) obtained from a fit of the data to the exchange theory cannot be reconciled with the line width of the relevant internal Raman mode. Hess and Prasad [4] studied the Raman line shape of the 764 cm^{-1} internal vibration in naphthalene and concluded that off-diagonal mixed mode quartic anharmonic interactions with 140 cm^{-1} lattice phonons were mainly responsible for the observed dephasing. The main problem with *both* theories, as Wertheimer [5] pointed out, is the fact that the excitonic nature of the vibrations studied was not accounted for. As a result only the self-correlation part [5] of the total vibrational correlation function was considered, as if the transition studied were a simple two-level-coupled-to-a-bath system.

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It therefore seems pertinent to study the simpler case of Raman dephasing in guest molecules in mixed molecular crystals where a two-level approach should be adequate. Our particular interest in this problem derives from results obtained previously [6] in a photon echo study of pure electronic and vibronic dephasing in mixed crystals. It was shown that optical dephasing was basically due to uncorrelated phonon scattering processes in the ground and electronically excited state involving a specific guest librational level. In the mixed crystal of pentacene in naphthalene [7] the frequency (ω) and lifetime (τ) of this libration were found to be rather different in the ground and electronically excited state. de Bree and Wiersma (dBW) [8] showed that in such a four-level-coupled-to-a-bath system optical Redfield relaxation theory should be used to interpret the homogeneous line shape. The pure dephasing constant $T_2^*(R)$ for such a four-level system takes the following form [8]:

$$1/T_2^*(R) = \tfrac{1}{2}[\tau_g^{-1} \exp(-\omega_g/kT) + \tau_e^{-1} \exp(-\omega_e/kT)] + \Gamma_{ge}^{(a)}, \quad (1)$$

where the subscripts g and e refer to the ground and electronically excited state, respectively. $\Gamma_{ge}^{(a)}$ refers to the adiabatic [8] contribution to T_2^{-1}. For the pure electronic and vibronic transitions in pentacene this contribution to T_2^{-1}, up to 20 K, was shown [7] to be negligible.

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In case of vibrational transitions one might expect [7] the ground and vibrationally excited state librations to be very close in frequency and lifetime, in which case, instead of eq. (1), exchange theory [2] should be used to describe dephasing. The exchange-determined dephasing constant $T_2^*(E)$ is given by.

$$1/T_2^*(E) = [\delta^2\tau/(1+\delta^2\tau^2)]\exp(-\omega/kT) + \Gamma_{ge}^{(a)}, \quad (2)$$

where $\delta = |\omega_e - \omega_g|$, $\tau = (\tau_e + \tau_g)/2 \approx \tau_e$ and $\omega = (\omega_e + \omega_g)/2 \approx \omega_e$. Note that exchange theory is only applicable when $\delta\tau \lesssim 1$. Furthermore in case of vibrational dephasing, in addition, τ should be much shorter than the vibrational relaxation time. For a thorough discussion of the limitations of exchange theory consult ref. [8]. Comparing eqs. (1) and (2) it is clear that in case of vibrational exchange, the homogeneous line shape is narrowed compared to the no-exchange case. In the extreme case, where $\omega_g = \omega_e$, exchange-induced dephasing will vanish and the adiabatic contribution ($\Gamma_{ge}^{(a)}$) to the homogeneous line shape will become very important.

With these facts in mind it seemed interesting to study vibrational dephasing in the well-characterized system of pentacene in naphthalene. The results reported here were obtained using resonance Raman scattering as a technique. Hochstrasser et al. [9] were the first to show that with this technique, in principle, vibrational dephasing could be studied. In the meantime we have also started time-resolved picosecond resonant CARS [10] and CSRS [11] experiments to obtain information on vibrational dephasing in the ground and electronically excited state. We note that some of the results communicated here were earlier reported in preliminary form [12].

2. Theoretical aspects of resonance light scattering

In a forthcoming paper [13] we will give a detailed account of some new theoretical aspects of resonance light scattering in a level system of the form depicted in fig. 1. Levels 1, 2, and 4 are, respectively, the ground state, the electronically excited state, and a ground-state vibrational level. Level 3 is the triplet state which may act as a bottleneck in the pumping cycle. The primed levels are librational levels superimposed on the unprimed ones. In a typical resonance scattering experiment a cw dye laser is used to near resonantly excite the transition $\langle 2| \leftarrow |1\rangle$, while the Raman (fluorescence) line shape near the transition $\langle 4| \leftarrow |2\rangle$ is being studied. Under spectral resolution, the following results were obtained [12] for the spectral line shapes of the fluorescence (a) and Stokes Raman (b):

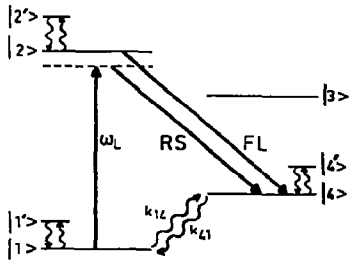

Fig 1. Typical level scheme appropriate to the study of resonance light scattering in a molecular mixed crystal. Levels 1, 2, and 4 are the ground state, the electronically excited state and a vibrationally excited state, Level 3 is the triplet state The primed levels are librational levels. RS stands for Raman Stokes and FL for fluorescence.

$$I_{24}^{FL}(\omega) \propto \Delta^{-2}\,\frac{2k_2^{-1} - T_2}{T_2}\,\frac{1/T_2'}{(\omega - \omega_{21} + \omega_{41})^2 + (1/T_2')^2}, \quad (3a)$$

$$I_{24}^{RS}(\omega) \propto \Delta^{-2}\,\frac{1/T_2''}{(\omega - \omega_L + \omega_{41})^2 + (1/T_2'')^2}. \quad (3b)$$

Note that eqs. (3a) and (3b) have been derived for homogeneous transitions. In these equations $k_2 = \gamma_2 - k_{2'2} \times k_{22'}/\gamma_{2'}$ is the rate for the *net* population loss out of level $|2\rangle$, and $\gamma_2 = k_{21} + k_{23} + k_{24}$. T_2, T_2' and T_2'' are the dephasing constants for the pure electronic, vibronic and vibrational transitions, respectively. These equations also show that both the Raman and fluorescence exhibit an inverse quadratic dependence on the magnitude of off-resonance (Δ) pumping. Furthermore, the integrated ratio (R) of the fluorescence over Raman $R = (2k_2^{-1} - T_2)/T_2$ can, in principle, be used to probe the electronic dephasing parameter [14]. If at low temperature $T_2 \to 2\gamma_2^{-1}$ then $R \to 0$ ($k_{22'} \to 0$ ($T \to 0$)). In case of resonance light scattering experiments on mixed crystals the effects of *inhomogeneous* broadening have to be taken into account. Eq. (3a) shows that the line shape of the fluorescence induced will suffer from both inhomogeneous broadening on the $\langle 2| \leftrightarrow |1\rangle$ and $\langle 4| \leftrightarrow$

|1⟩ transition, while the Raman line shape is only sensitive to inhomogeneous broadening at the Raman transition itself.

When the inhomogeneous broadening of different transitions is assumed to scale as their dispersion shifts, the inhomogeneous broadening of Raman transitions is expected to be only a fraction of the inhomogeneous broadening of the pure electronic transition. This implies that in mixed molecular crystals one may expect the Raman line shape to reflect only homogeneous vibrational dephasing effects.

3. Experimental

The mixed crystals of pentacene in naphthalene were grown from the melt using a Bridgman furnace. All experiments were performed on crystals cut along the *ab* cleavage plane. The pentacene concentration was such ($\approx 10^{-6}$ M/M) that the origin peak OD was ≈ 1. A Spectra Physics model 580 single mode dye laser was used to observe the near resonance Raman scattering. During an experimental run the dye-laser frequency stability was ≈ 100 MHz as checked with a Tropel 240 confocal scanning interferometer. The dye-laser beam was externally stabilized [15] and mechanically chopped The scattered radiation was collected at 90° to the incident excitation light and passed through appropriate Corning filters. The light was then passed through a Spex Ramalog 6 double monochromator and phase-sensitively detected using a photomultiplier.

The temperature of the crystal was measured with an accuracy of about 0.1 degree using a calibrated Rh–Fe resistor in contact with the sample.

4. Results and discussion

Fig. 2 shows a typical high-resolution (0.16 ± 0.01 cm^{-1}) light scattering spectrum of pentacene in naphthalene at 1.6 K, showing both the broad fluorescence and sharp (unresolved) Raman signal, involving the 993 cm^{-1} pentacene a_{g-} vibrational mode. Note that the appearance of a fluorescence signal at this temperature implies, through eq. (3a), that at 1.6 K, $T_2 < 2T_1$, in agreement with a photon echo report from the Fayer group [16]. The slit corrected (by deconvolution) Raman line width at this temperature was determined to be 0.14 ± 0.02 cm^{-1}, almost a factor of 10 narrower than the corresponding fluorescence signal. This Raman line width, for a lorentzian line shape profile, corresponds to a vibrational dephasing T_2 of 76 ± 10 ps. For the Raman transition unto the 753 cm^{-1} mode, a line width of 0.10 ± 0.02 cm^{-1} was determined which corresponds to a vibrational T_2 of 106 ± 25 ps. A picosecond time-resolved resonant CARS experiment [17] at the same temperature on this 753 cm^{-1} vibrational transition exhibited exponential decay (thereby confirming the lorentzian "homogeneous" line shape) with a lifetime ($\frac{1}{2}T_2$) of 55 ± 5 ps. The good agreement between both measurements lends credibility to the analysis of the Raman line shape as presented here. We further note that for the 753 and 993 cm^{-1} mode the same vibrational T_2 values were obtained from frequency line-narrowing experiments [18]. We interpret these low-temperature vibrational T_2 as solely being caused by *vibrational* relaxation [19]. The vibrational relaxation times at 1.6 K of the 753 and 993 cm^{-1} mode are thus, respectively, 55 ± 5 ps and 38 ± 5 ps

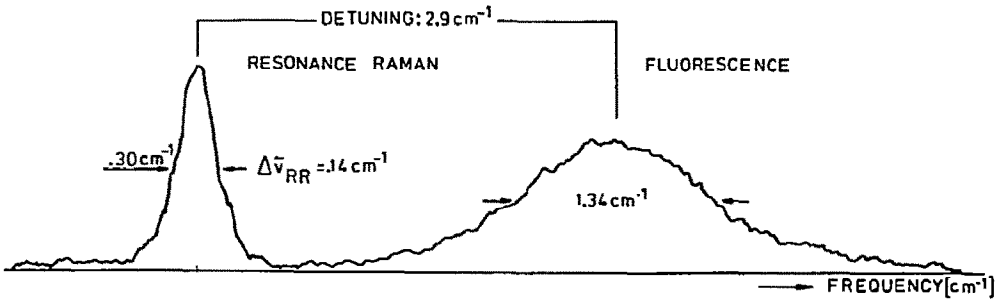

Fig. 2 Typical high-resolution light scattering spectrum (bandpass 0 16 ± 0 01 cm^{-1}) of pentacene in naphthalene at 1.6 K. (2 mW excitation power.)

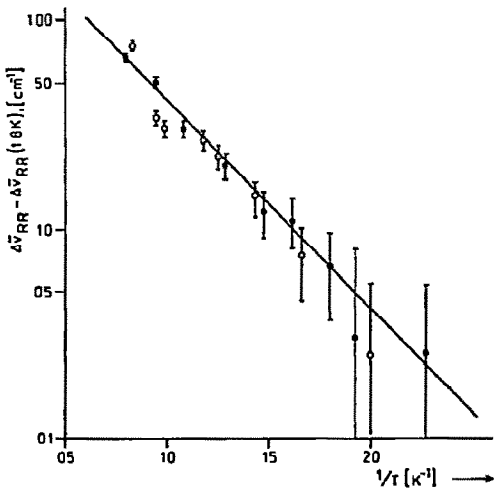

Fig. 3 Temperature dependence of the pure dephasing part $(\pi T_2^*)^{-1}$ of the homogeneous line width of the 753 cm^{-1} (solid circles) and 993 cm^{-1} (open circles) vibrational transitions of pentacene in naphthalene. The solid line is a fit to the near resonance Raman data as explained in the text.

Fig. 3 shows for both the 753 and 993 cm^{-1} mode the activation of the pure dephasing-induced part of the Raman line width $(\pi T_2^*)^{-1}$ with temperature. Here

$$1/T_2^* = 1/T_2 - 1/2T_1, \quad (4)$$

with T_1 the vibrational relaxation lifetime, which is assumed [19] to be temperature independent. We first note that at the highest temperature (12 K), where reliable Raman data could be taken, the Raman line width of both modes is a factor of 2 *broader* than the homogeneous line width of the pure electronic transition [7]. This indicates that vibrational dephasing in this mixed crystal supersedes electronic dephasing. This sharply contrasts the findings reported by Hochstrasser et al. [9] on the system azulene in naphthalene where at 30 K, the Raman line width of a 825 cm^{-1} vibrational mode was at least 10 times narrower than the line width of the pure electronic transition.

Despite appreciable scatter in the low-temperature data of fig. 3, it is clear that vibrational dephasing of these modes is exponentially activated. Using the substitution

$$T_2^*(T) = T_2^*(\infty)\exp(\Delta E/kT), \quad (5)$$

which is consistent with either eq. (1), when $\omega_g \approx \omega_e$ and $\tau_g \approx \tau_e$, and eq. (2) for $\Gamma_{ge}^{(a)} = 0$, we obtain from a fit to the data $\Delta E = 17.0 \pm 3$ cm^{-1}, $T_2^*(\infty) = 2.4 \pm 1.5$ ps. From photon echo experiments on the pure electronic transition of pentacene in naphthalene [7] we concluded that the librational mode in the ground state had a frequency of 18.0 cm^{-1} and a lifetime of 3.5 ps.

From the close correspondence between these numbers we conclude that vibrational dephasing in the 753 and 993 cm^{-1} modes of pentacene is caused by *uncorrelated* phonon scattering processes in the ground and vibrationally excited state. Vibrational dephasing, as pure electronic dephasing, in this system thus should be described using Redfield relaxation theory [eq. (1)] rather than exchange theory [eq. (2)].

The frequency difference (δ) of the libration in the ground and vibrationally excited states must therefore be at least 1.52 cm^{-1} ($\delta > \tau^{-1}$). This shows that the diagonal quartic vibration–phonon anharmonic coupling can decouple the fundamental and hot vibrational transition in mixed crystals. The conclusion then must be that vibrational exchange is not a general characteristic of vibrational transitions in molecular solids.

We admit that much remains to be learned about the energetics and dynamics of pseudolocalized phonons (librations) in mixed molecular crystals. Molecular dynamics calculations on these systems are expected to be enlightening.

We conclude this paper by noting that the interpretation presented here would become undisputable if vibrational dephasing in the excited state of pentacene would conform to our expectations based on the known excited-state librational frequency and lifetime. Time-resolved CARS and CSRS experiments are underway to improve on the data presented here and to study (excited-state) vibrational dephasing in this and other mixed crystal systems.

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Note added in proof

It has come to our attention that Andrews and Hochstrasser [20] recently reported a Raman dephasing study, using resonant coherent Stokes generation, of the system pentacene in benzoic acid. Up to 20 K they find no broadening of the Raman lines, in sharp contrast to the findings reported in this letter for pentacene in naphthalene. It seems plausible that in the pentacene in benzoic acid system, the dephasing channel involving librations is blocked through resonant exchange [($\delta = 0$ in eq. (2)]. We are presently studying the low-temperature dephasing in this system by picosecond delayed CARS.

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